ACYLAZIRIDINE REACTIVITY IN THE LINER AND PROPELLANT ENVIRONMENTS

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ABSTRACT

In order to clarify the mode of action of acyleziridine bond promoters, a monofunctional acylaziridina was synthesized and the reactivity of this model compound with 1-propanol in the presence and absence of ammonium perchlorata was studied. The major prooess identified involved ring-opening of the aziridine ring by the alcohol to give isomeric amidea. Following this study, the reactivity of the model bond promoter with hydroxyl terminated polybutadiana polymers was investigated employing carbon-13 nuclear magnetic resonance spectrometry as the primary analytical tool.

INTRODUCTION

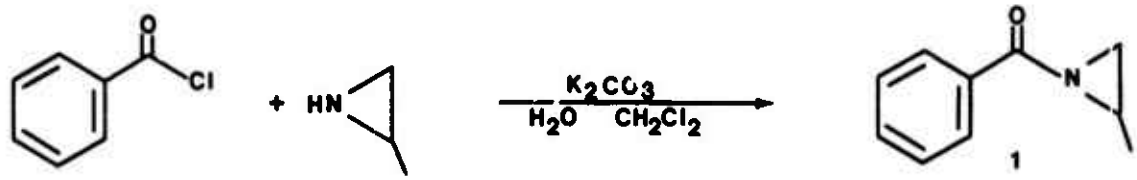
Compounds containing the acylaziridine group auch as HX-752 and HX-868 have been extensively employed as bonding agents in HTPB propellants and as bond promoters in liner formulationa. Despite the widespread use of these reagents, surpriaingly few studias have been reported concerning the mode of action and reactivity of thia class of compounds in the HTPB propellant and liner environments. [1-6] Prior experiments oonoerning the reactivity of acylaziridines were directad toward the behavior of these reagents in CTPB polymer systems. [7, 8] Since CTPB polymers are more acidic and lesa nucleophilic than the modarn HTPB polymars, the extension of data obtained on CTPB polymera to HTPB polymera may yield arroneous conclusions.

The study of acylaziridine bond promoter reactivity and mode of aotion could be attempted by investigating the cure chemistry of a perticular propellant, but this approach yields aerious analyticel prcblems. The produots obtained in such a study would be part of a complex polymer system making the identification and quantification of reaction products a most formidable and time-conauming task. In auch situetions, one ia often reduced to merely obaerving atarting materiala disappear with little knowledge of the reaction produota. A second approach is the design of a model aystem that accurately mimics the propellant ingredients with monofunctional compounds. The major advantage of suoh a system is that distinct, isolable, reaction products will be formed, greatly aimplifying the analytioal procaes. The development and atudy of such a model aystem is tho approaoh we selected.

SYNTHESIS OF THE MODEL BOND PROMOTER AND REFERENCE COMPOUNDS

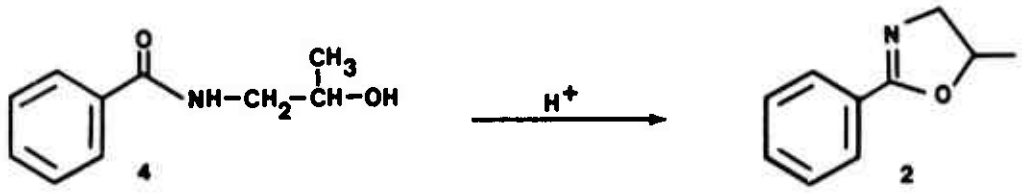
The model bond promoter seleoted for this atudy was 1-benzoyl-2-methylaziridine(1). This compound possesses tha requirad conjugated acylaziridine group and is monofunctional. The presence of the methyl substituent on the aziridine ring adda aome complioation due to the possibility of isomer formation, but it is required for a good model aystem since the atability and reactivity of small ring systems are aubatantially affected by ring subatitution. Tha methyl substituent alsc servas as a label whose location in the reaction produots will provide information concerning the mechanism of the various reaction pathways. This mechanistic detail would not be available if a model compound with fewer aubstituents were employad in this study.

The model compound was prepared by the Schotten-Baumann reaction of benzoyl ohloride with 2-methylaziridina as shown below. This reaction gava tha model compound (1) in 93% yield after distillation (B.P.=61-62°C at 0.06 Torr) and of 98% purity as estimated by NMR spectrometry. Further purification could be accomplished by column chromatography on silica gel employing dichloromethane as the aluent.

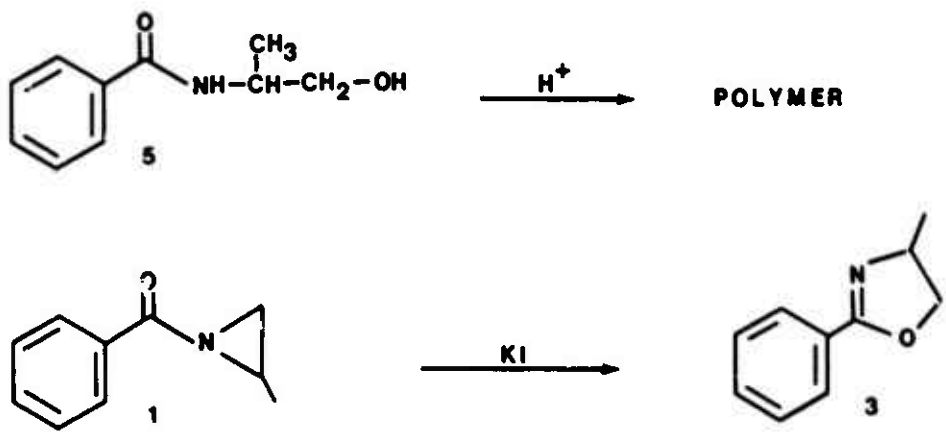


Having the desired model compound in hand, our efforts turned to preparation of 5-methyl-2-phenyloxazoline (2) and 4-methyl-2-phenyloxazoline (3). Aoylaziridines are known to form oxazolines on heating, treatment with acids or halide salts, and it was desirable to have authentic samples of these two isomers (2 and 3) to allow unambiguous structural assignments.

The synthesis of 5-methyl-2-phenyloxazoline (2) is outlined below and began with the Schotten-Baumann reaction of benzoyl chloride with 1-amino-2-propanol to give the amide 4 in 64% yield after recrystallization (m.p.=92.5-95.5°C). This material was converted to the desired oxazoline by dehydration with p-toluenesulfonic acid in refluxing toluene to give 2 in 44% yield. The yield for this reaction was low, but sufficient material was obtained for characterization and no attempt was made to optimize the yield.



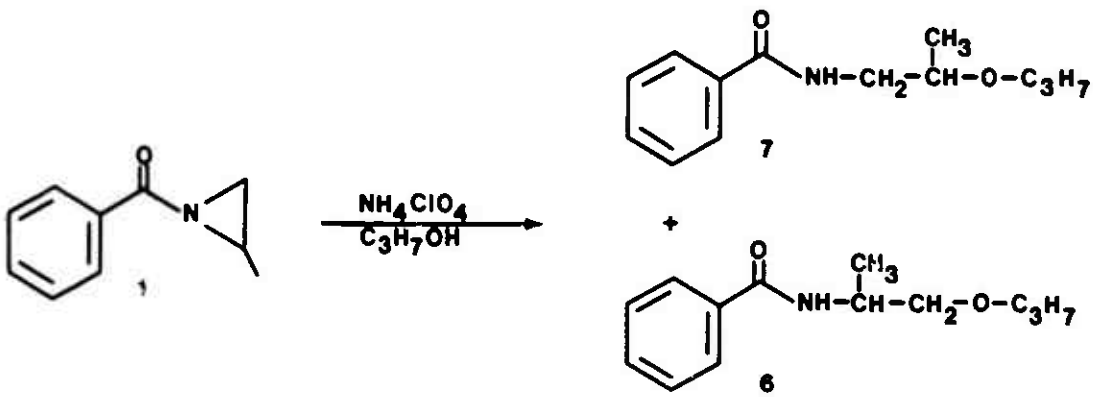
The initial attempt to prepare 4-methyl-2-phenyloxazoline (3) followed the route described above for the isomeric oxazoline 2. Unfortunately, attempted dehydration of the amide 5 led only to polymer formation. The successful method for the preparation of 3 involved the potassium iodide catalyzed rearrangement of the model compound 1 in acetone at room temperature. Treatment of 2-alkyl substituted N-acylaziridines is known to yield 4-alkyl substituted oxazolines; thus, the acylaziridine 1 on treatment with potassium iodide gave 4-methyl-2-phenyloxazoline (3) in 95% yield.[7] The material obtained was 95% pure, contaminated with 5% of the 5-methyl isomer (2).



CHARACTERIZATION OF GENERAL REACTIVITY

The initial characterization of reactivity involved determination of the reactivity of the model bonding agent with alcohols. The alcohol employed, 1-propanol, contains a primary hydroxyl group (as are the majority of the hydroxyl groups in the HTPB polymer) and has a boiling point high enough to allow reaction temperatures as high as 97°C. In addition, this alcohol is water soluble providing a simple method for its removal from reaction mixtures.

The first set of reaction conditions investigated were designed to favor reactions between the alcohol and acylaziridine. Thus, the model compound was treated with an excess of 1-propanol in the presence of ammonium perchlorate at 65°C. Under these conditions, the model compound was consumed in less than four hours. The NMR, IR, and mass spectra of the crude reaction mixture showed this material to be mainly products 6 and 7 resulting from ring-opening of the acylaziridine by 1-propanol as shown below. In addition, small amounts of the oxazolines 2 and 3 were present. The upfield region of the 200 MHz NMR spectrum of a typical reaction mixture is shown in Figure 1a. The small doublets centered at 1.37 and 1.31 ppm are due to the oxazolines 2 and 3 respectively. The triplet at 0.93 ppm and the sextet centered at 1.59 ppm as well as the doublets centered at 1.18 and 1.29 ppm are assigned to the amides 6 and 7.



The relative positions of the two methyl doublets at 1.14 and 1.25 suggest that the major component of the mixture is the isomer 7. This assignment was verified by the carbon-13 and mass spectra of the reaction mixture. The proton coupled and decoupled carbon-13 spectra are shown in Figure 2. The two resonances at 69.2 and 72.7 ppm are due to the carbons adjacent to the ether oxygen and their multiplicity in the proton coupled carbon-13 spectrum is consistent only with the isomer 7 being the major component. The concentration of the four components was determined by integration of the proton spectrum and are shown in Table 1, entry 1.

The second set of reaction conditions investigated involved an acylaziridine to 1-propanol ratio that more closely resembled the ratio found in a typical propellant formulation. Thus, a ratio of 1-propanol to acylaziridine of 2.7:1 was used with the ratio of acylaziridine to ammonium perchlorate equal to 1.4. This mixture was stirred at 65°C for four hours. The upfield portion of the NMR spectrum of the material obtained is shown in Figure 1b. Integration of this spectrum gave the results shown in Table 2, entry 2. Once again, the amide 7 was the major product (83%) with minor amounts of the isomer 6 (6%). In addition to 6 and 7, 9% of the oxazoline 2 and 2% of the oxazoline 3 were also present.

An investigation of the reactivity of the model bond promoter 1 with 1-propanol in the absence of ammonium perchlorate was also conducted. This experiment was directed toward a better understanding of the behavior of acylaziridines in the liner environment. Treatment of 1 with excess 1-propanol at 65°C for one week resulted in the reaction of 62% of the starting acylaziridine 1. In addition to the starting material, 45% of the amide 7, 12% of the amide 6, 2% of the oxazoline 2, and 3% of the oxazoline 3 were present (see Table 1, entry 3).

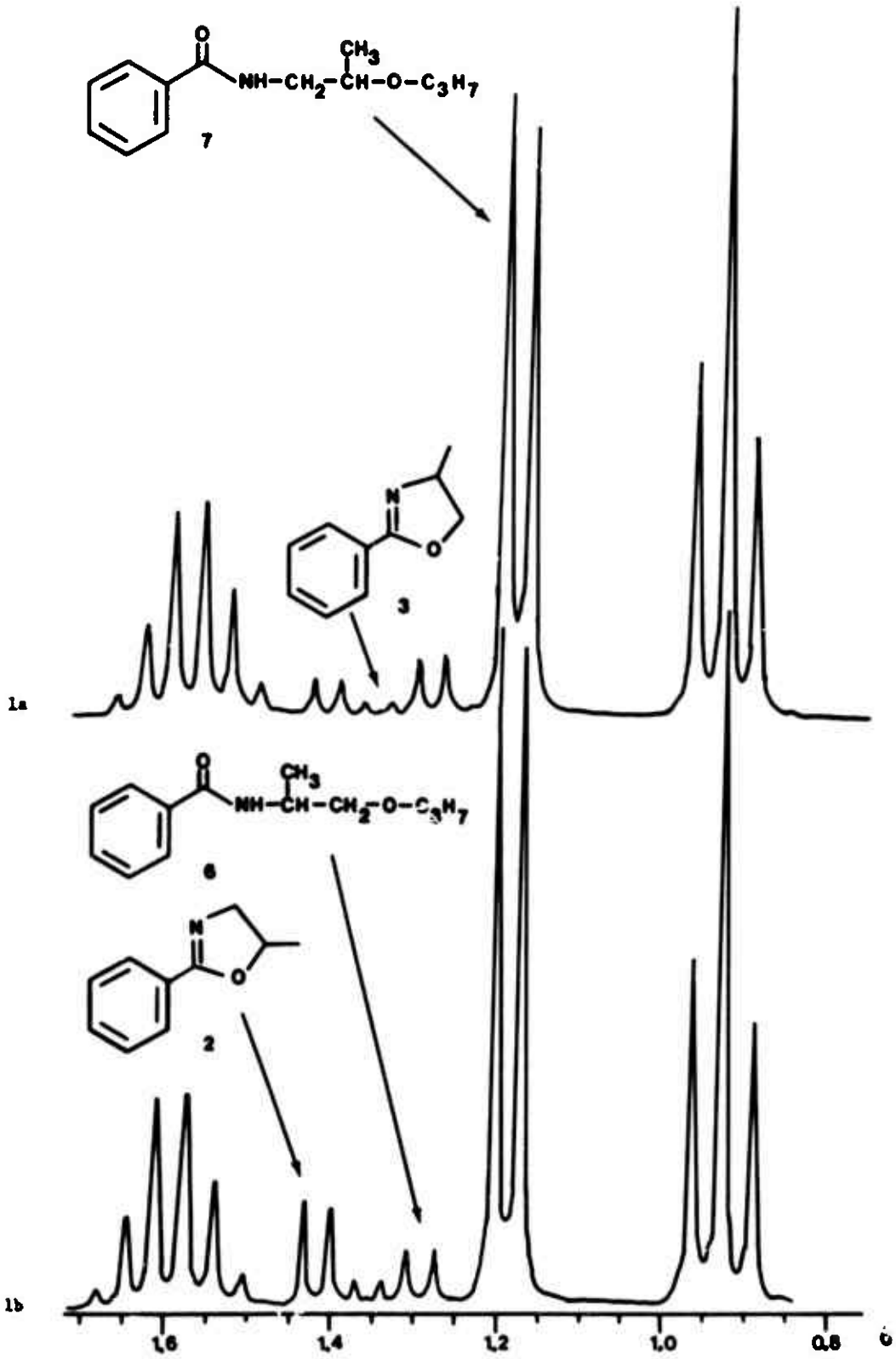


Figure 1 200 MHz Proton NMR Spectra of 1-Propanol Addition Products

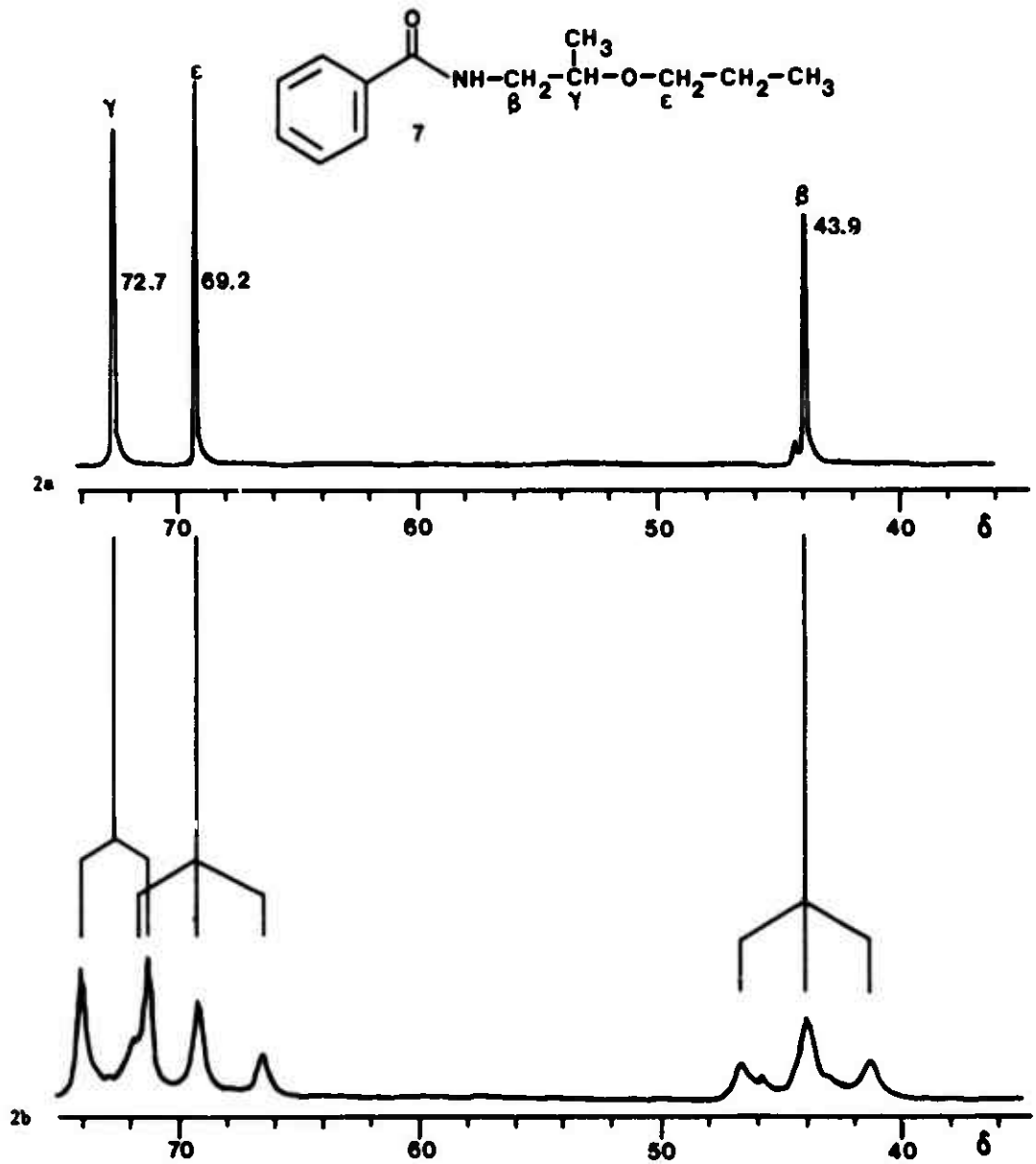


Figure 2 Carbon 13 NMR Spectra of the 1-Propanol Addition Product. (2a - Decoupled Spectrum; 2b - Coupled Spectrum)

Table I. Product Ratios for 1-Propanol Reactivity Studies

ENTRY	1-Propanol / Aziridine	AP / Aziridine	1	2	3	6	7
1	25.0	0.63	0	4	1	7	88
2	2.7	0.69	0	9	2	6	83
3	24.0	0	38	2	3	12	45

A second reaction pathway that may be available to acylaziridines in the liner and propellant environments is reaction with isocyanate curing agents. Simple N-acyl substituted aziridines are known to react with isocyanates at temperatures between 100-170°C to yield substituted imidazolidones as shown below. [9] The mechanism of this reaction is likely to involve ring- opening to the acylaziridine to yield a zwitterion intermediate that reacts with the isocyanate to give the observed products. Since the environment at the propellant to liner interface is quite polar, it was thought that such reactions may be possible. Treatment of the model compound 1 with phenyl isocyanate in the presence and absence of ammonium perchlorate did not give addition products.

The reactivity of the oxazolines 2 and 3 was assessed to determine their stability under the reaction conditions. Perchlorate salts of oxazolines are known to polymerize on heating and anhydrous hydrochloride salts of oxazolines have been shown to rearrange to -chloroamides. [10, 11] Additional possible reactions include acid catalyzed ring opening by 1-propanol and hydrolysis of the oxazoline by water absorbed on the ammonium perchlorate. [12,13]

The reactivity tests were carried out by treating one equivalent of the oxazoline (2 or 3) with forty equivalents of 1-propanol and ammonium perchlorate (2.7 equivalents). The resulting mixture was stirred at 65°C for one week at which time the reaction mixture was worked up and analyzed by NMR. In both cases, no reaction was observed, only unreacted oxazoline was recovered.

DISCUSSION OF 1-PROPANOL REACTIVITY STUDIES

As can be seen by inspection of Table I, the major process under all conditions results from alcohol addition to the aziridine ring of 1 to give the amides 6 and 7. Comparison of entries 1 and 2 shows that the product distribution is only slightly affected by the alcohol concentration and that decreased alcohol to aziridine ratios give a higher amount of oxazoline 2 at the expense of amide 7. Also, the amounts of the products 2 and 6 are very similar for entries 1 and 2. The data given in entry 3 shows that alcohol addition to the aziridine is the major process even in the absence of ammonium perchlorate. Thus, ammonium perchlorate accelerates the reaction rate, but has only a small effect on the product distribution.

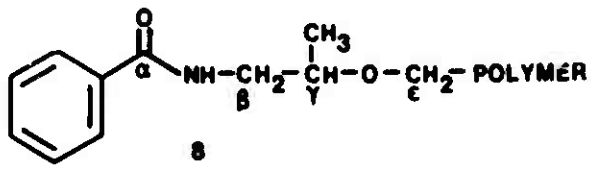
These data demonstrate that a major pathway available to acylaziridines in HTPB systems is reaction with Hydroxyl groups to yield amides. It is also important to note that the products shown in Table I account for the majority of the acylaziridine consumed. Mass balance considerations limit the amount of acylaziridine homopolymerization to be less than 15%. Thus, a possible mode of action of acylaziridine bonding agents and bond promoters involves cross linking of the polymer network through reaction with free HTPB hydroxyl groups.

REACTION OF R-45M HTPB POLYMERS

The eeoond phase of thia study involved the determination of the reactivity of the model bond promoter 1 with the R-45M HTPB polymer employed in propellant formulations. The study of HTPB polymer reactivity is complicated by the fact thet the polymer has an average molecular weight of approximately 2800 and a funotionality slightly over 2 hydroxyl groups per molecule. Since the R-45M polymer reactivity ia reatrioted to hydroxyl reaotiona, and theee hydroxyl groups are preaent only in very low concentrations, the analytical procesa ie very difficult.

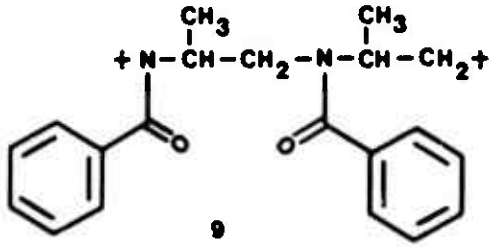
Our epproaoh to the aolution of the anelytical problems involved the uae carbon-13 NMR apectrometry. While C-13 NMR is not noted for senaitivity, it offere the advantage that the oarbon atoms adjaoent to the hydroxyl groupa can be direotly obeerved. The aeneitivity problems were overcome by using a relaxation reagent permitting more rapid spectral acquisitions end the use of 20mm sample tubea. It ehould be noted that our goal for thie phase of the study waa to define reactivity trenda and not to obtain quantitative dsta.

The initial stage of thia atudy involved the oharacterization by C-13 NMR of the reaction producta obtained in the 1-propanol reactivity atudiea (3ee Tabl. II).[16] The amide 7 ehould aarve aa a reaeonably good model for the reaction product of the model bonding agent and the R-45M polymer (8) as ehown below. The chemical shifts of the α, β, γ, end ε carbons of 7 should be very aimilar to the R-45M reaction product 8.



8

Homopolymers of the bond promoter such aa 9 can alao be identifiad by C-13 NMR. The C-13 apeotrum of 9 haa been raported and a portion of tha deta are shown in Tablo II. [14] The C-13 apectrum of tha R-45M polymer has been previously reportad and our data on thia polymer are in good agreement with the literature data. [15] Tha isomeric R-45M tarminal carbons azhibit C-13 peake at 58.2, 63.5, and 64.8 ppm (saa figure 3a).



9

The firet axperiment involved treatment of R-45M (14.1g) with ammonium perchlorata (3.0g) and the modal bond promotar (2.0g). Thie mixture was etirred et 65°C. The reeotivity of the model bond promoter was much elower than observed with 1-propanol; efter 196 hours, the modal bond promoter waa not totally consumed. The tarminal carbon region of the C-13 NMR apectrum of the matariel obtained from this experiment is shown in figure 3b.

The three peaka due to unreacted R-45M ere present along with a major peak at 61.1 which ia assigned to be the oxazoline 2. There is also e perk et 163.4 which is alao asaigned to the oxazoline 2. The two peaks at 68.9 and 72.8 are aasigned to be tha and carbona of tha eddition product 8. The carbonyl carbon of 8 at 166.9 providea additional aupport for assignment of the amida 8. An additional peak et 178.6 is due to unreected model bonding agent. A very rough aetimation of tha ratio of tha compounds 1, 2, and 8 is 20%, 30%, and 50% raapectively. Significantly, no peeks conaiatent with the homopolymer 9 were present in thia apectrum.

A second reactivity study involved heating a mixture of R-45M (7.7g) with the model bond promoter 1 (1.0g) at 65°C for 700 hours. No reaction was observed by C-13 NMR.

MECHANISTIC CONSIDERATIONS

A reaction manifold for the model bond promoter is shown in Figure 4. In the presence of 1-propanol ($R=C_3H_7$) and ammonium perchlorate, the amide 7 was major product. This demonstrates that the mechanism for this reaction involves a carbonium ion intermediate. Initial protonation of 1 followed by ring opening would give the most stable carbonium ion 10. This ion (10) then partitions between reaction with propanol to give 7 or intra-molecular ring closure to give the oxazoline 2. In the absence of ammonium perchlorate, the formation of ion 10 is slowed, and the amide 6 becomes a more important product as shown in Table I.

The use of R-45M as the alcohol in place of 1-propanol yields reaction rates that are significantly decreased. This is probably caused by the decreased polarity of the R-45M polymer as compared to 1-propanol and by the decreased solubility of ammonium perchlorate in R-45M. The reduced rate gives added support for the carbonium ion pathway. In the presence of R-45M, ring closure of the carbonium ion 10 is faster than hydroxyl attack to give the oxazoline 2 as the major product. The second major product is the amide 8 resulting from ring opening of the acylaziridine by the hydroxyl groups of the R-45M polymer.

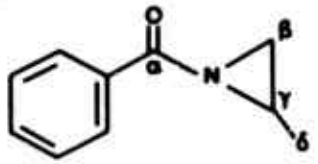
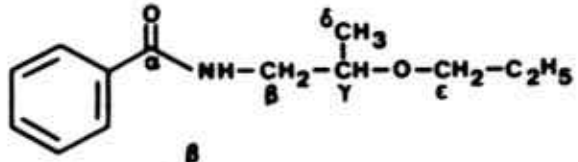
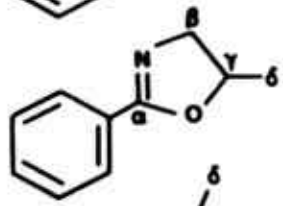
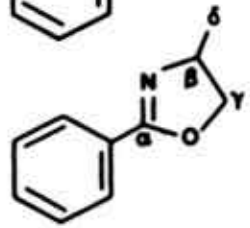
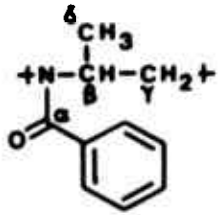
CONCLUSIONS

This study has demonstrated that an important reaction pathway for acylaziridine bond promoters and bonding agents in the HTPB propellant environments involves reaction with the hydroxyl groups of the polymer. The rearrangement of acylaziridines to oxazolines was also identified as a major process. Significantly, homopolymerization of the model bonding agent was not identified as a major process. These data suggest that these reagents function by increasing the local crosslink density of the propellant in the area adjacent to the ammonium perchlorate particles through reaction with hydroxyl groups of the polymer.

In addition, this work has provided information concerning the mechanism of amide and oxazoline formation. The structures of the major products suggest that the predominant process involves formation of a carbonium ion that is either captured by alcohol to give amides or closes to yield oxazolines. This carbonium ion pathway is reasonable since the propellant ingredients provide a very polar environment that will favor ionic pathways.

In conclusion, this study has demonstrated the value of an experimental approach that begins with simple, easily defined systems and graduates to the more complex cases. The application of this approach has significantly improved our understanding of acylaziridine reactivity in the liner and propellant environments.

Table II. Carbon - 13 NMR Data for Selected Compounds

STRUCTURE	α	β	γ	δ	ε
	179.1	32.1	34.4	17.6	–
	166.3	43.9	72.7	16.6	69.2
	163.6	61.4	76.2	21.1	–
	163.3	61.9	74.0	21.3	–
	171.2	53.6	46.0	16.0	–

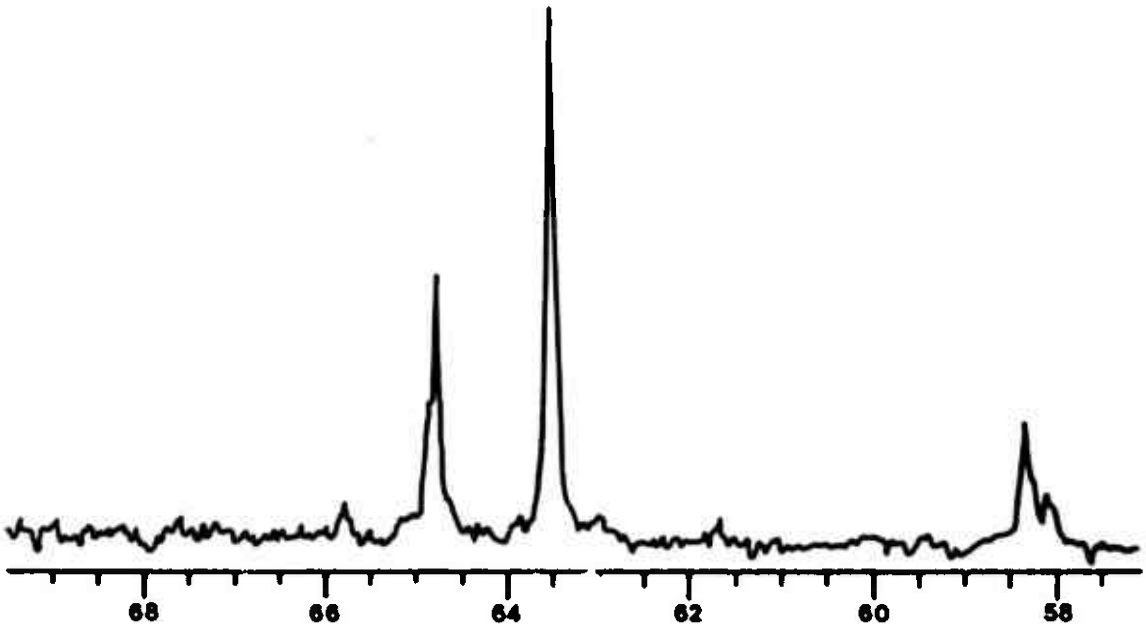


Figure 3a Terminal Carbon Region of the C-13 NMR Spectrum of R-45M Polymer

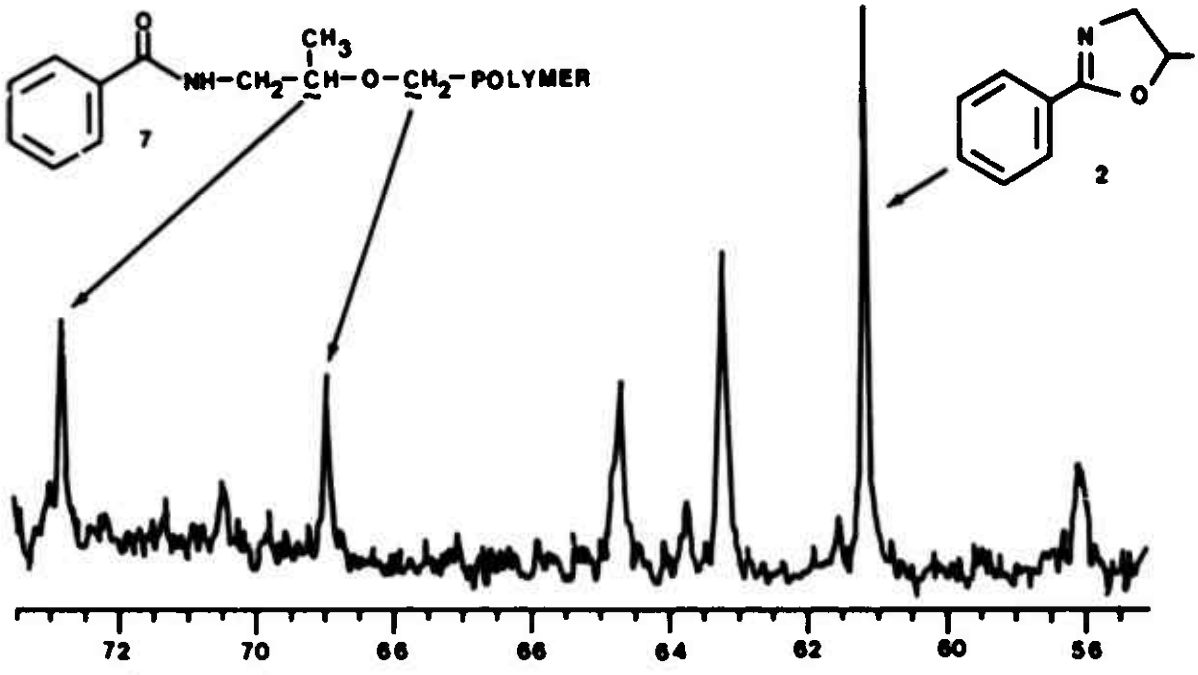


Figure 3b Terminal Carbon Region of the C-13 NMR Spectrum of the R-45M Reaction Product

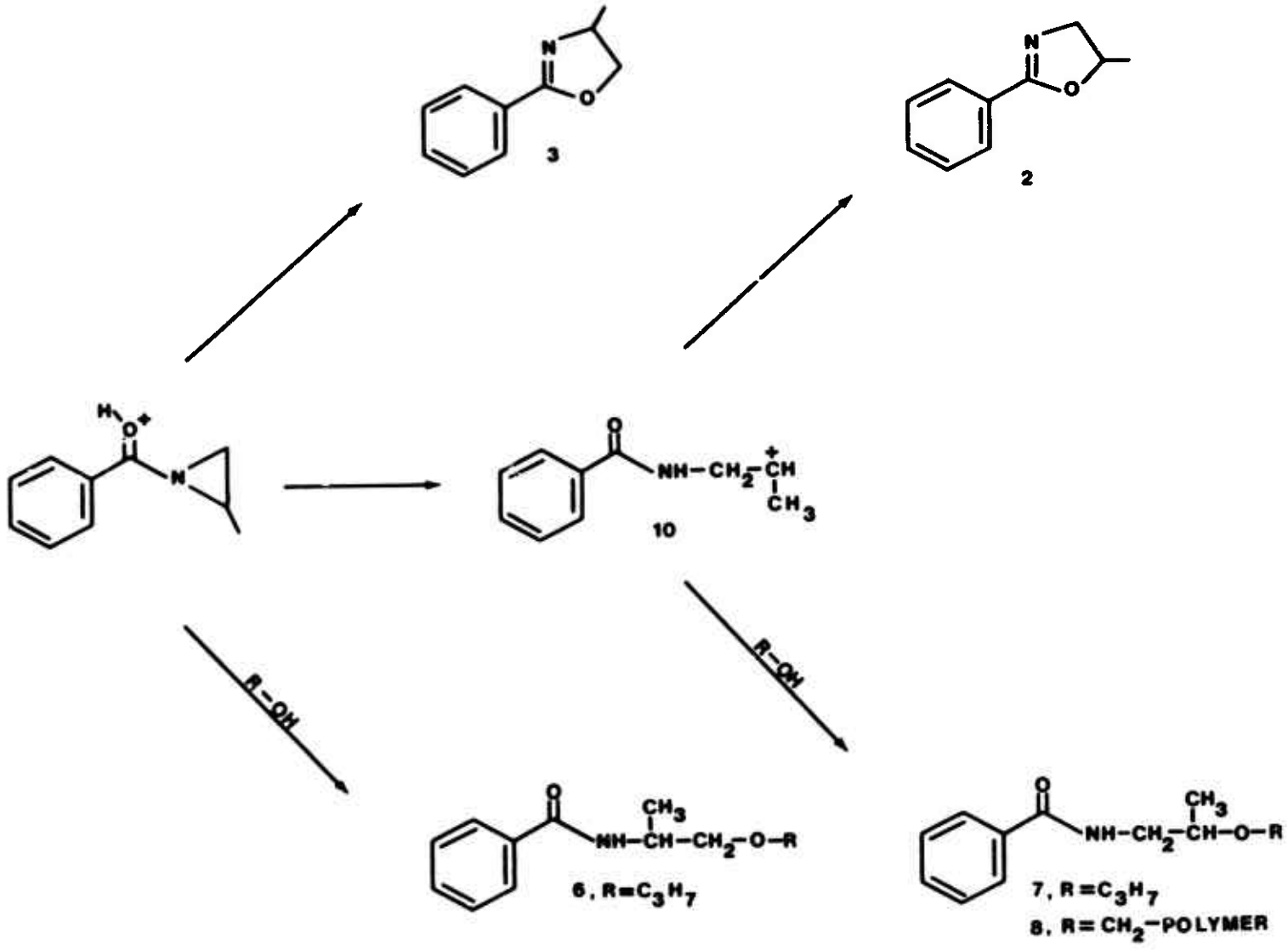


Figure 4 Reaction Manifold for the Model Bond Promoter

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16. Carbon -13 NMR spectra were obtained at 50 MHz in deutariochloroform. Chemical shifts are referenced to the center line of deutariochloroform at 77.0 ppm.